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Abstract

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SYNTHESIS OF VINYL CHLORIDE BY CHLORINATION OF ETHYLENE IN A FLUIDIZED BED OF CATALYST

It is generally known that the halogenation of lower unsaturated hydrocarbons in principle proceeds according to two types of reactions that differ from one another: in one case the reaction proceeds with saturation of the double bond, i.e., with formation of dihalogen derivatives; in the other case, substitution of the hydrogen atom located at the double bond by a halogen atom occurs. As a result of such a substitution reaction, monohalogen-substituted unsaturated hydrocarbons are formed. Examples are vinyl chloride from ethylene, allyl chloride from propylene, etc. Substitution chlorination of unsaturated hydrocarbons depends on two factors: the structure of the olefin and the reaction temperature. Olefins of normal structure at room temperature or at a somewhat higher temperature form only addition products. Iso-structure olefins under the same conditions form products of substitution chlorination. The latter question has been described in the literature in rather great detail ([1–7]).

Substitution chlorination of olefins of normal structure has been studied comparatively little. It is known that it proceeds at higher temperatures, on the order of 250–500°. Thus, in the chlorination of ethylene at 400° over aluminum or copper chloride catalysts, the resulting mixture contained (in %): vinyl chloride 21.9, ethyl chloride 45.9, methyl chloride 3.7 ([8]).

It should be noted, however, that at high temperatures a considerable portion of the ethylene undergoes destructive chlorination. Several methods have been proposed for suppressing destructive chlorination: dilution of the gas mixture with inert gases and the use of a large excess of ethylene. It has been established ([9]) that as the degree of dilution of ethylene increases, the amount of substitution-chlorination products increases. For example, at nitrogen : ethylene ratios of 4 : 1, the yield of vinyl chloride at 346° reaches 52.7%. At higher temperatures, for example at 485°, intense destructive chlorination takes place regardless of the degree of dilution.

Relatively good results are obtained when chlorination is carried out with a large excess of ethylene. Thus, at an ethylene : chlorine ratio of 6.6 : 1 and a temperature of 400°, the yield of vinyl chloride reaches 98.5% (^{10}). In this case, it is recommended that only the initial gaseous components be preheated at 400°. According to V. N. Antonov (^{11}), when chlorination is carried out in a medium of molten salts it is possible to reduce the ethylene : chlorine ratio to a considerable extent—to 2.5 : 1. The degree of destructive chlorination is somewhat slowed in the presence of such compounds as hydrogen sulfide, hydrogen selenide, or hydrogen telluride.

The degree of substitution chlorination is greatly influenced by the presence in the initial gas mixture of certain substances, for example oxygen, tetraethyllead, and dichloroethane (^{13}). It has been found that, at a content

in a gas mixture containing 0.5% oxygen, the yield of vinyl chloride reaches 93% (^{9}). The presence of saturated hydrocarbons in ethylene, on the contrary, sharply retards substitution chlorination. Thus, when the ethylene contains about 15% ethane, the conversion of chlorine decreases from 95 to 14.5% (^{14}).

Thus, high-temperature chlorination, irrespective of the degree of dilution and the excess of ethylene, is constantly accompanied by destructive chlorination. The main reason for this is the high temperature. According to V. N. Antonov, raising the reaction temperature from 390 to 450° leads to a 20-fold increase in soot formation. Under these conditions an excess amount of ethylene does not reduce the degree of destructive chlorination (^{11}). In this respect, carrying out the process in a fluidized bed of catalyst is of definite interest. Moreover, it was shown for the lower alkanes (^{15}) that under fluidized-bed conditions combustion is almost not observed.

Pumice was used by us as the heat carrier. Chlorination was carried out at a temperature of 450°. The data obtained are given in Tables 1 and 2. As can be seen from the data in Table 1, under the indicated conditions relatively high yields are obtained at ethylene : chlorine ratios of 3 : 1 and 4 : 1. Table 2 gives data on the composition of the products of the ethylene chlorination reaction.

Table 1

Conditions for obtaining vinyl chloride

No.	Passed, liters: C_2H_4	Passed, liters: Cl_2	C_2H_4:Cl_2	Space velocity	Linear velocity	Conversion of ethylene	Conversion of chlorine	Yield of vinyl chloride on reacted C_2H_4	Yield of vinyl chloride on reacted Cl_2
1	110.0	36.7	3 : 1	180.0	0.016	69.3	100.0	74.1	51.3

No.	Passed, liters: C_2H_4	Passed, liters: Cl_2	C_2H_4:Cl_2	Space velocity	Linear velocity	Conversion of ethylene	Conversion of chlorine	Yield of vinyl chloride on reacted C_2H_4	Yield of vinyl chloride on reacted Cl_2
2	110.0	36.7	3 : 1	180.0	0.016	71.3	100.0	74.8	53.3
3	141.1	35.1	4 : 1	174.1	0.015	81.5	100.0	76.8	62.6
4	110.0	27.5	4 : 1	169.0	0.015	75.8	100.0	71.4	54.9
5	166.0	35.5	4.6 : 1	188.5	0.014	54.3	100.0	57.8	31.4
6	166.0	35.5	4.6 : 1	191.7	0.017	62.6	100.0	67.0	41.9

Table 2

Composition of the products of the ethylene chlorination reaction

No.	Catalyst weight, g	Vinyl chloride, g	Vinyl chloride, %	Ethyl chloride, g	Ethyl chloride, %	Vinylidene chloride, g	Vinylidene chloride, %	Dichloroethylene, g	Dichloroethylene, %	Trichloroethylene, g	Trichloroethylene, %	Dichloroethane, g	Dichloroethane, %	Trichloroethane, g	Trichloroethane, %
1	77.2	52.6	62.8	2.2	2.8	9.4	12.2	4.9	6.4	1.5	1.9	5.1	6.6	1.5	1.9
2	80.3	54.7	68.0	2.0	2.5	11.5	14.3	4.7	5.8	1.4	1.7	4.8	5.9	1.4	1.8
3	91.5	61.1	67.2	3.1	3.4	8.3	9.1	2.8	3.1	7.4	8.1	7.9	7.8	1.2	1.4
4	71.6	51.6	72.2	1.9	2.6	6.7	9.4	2.2	3.1	4.3	6.0	4.1	5.7	0.7	1.0
5	57.9	31.1	53.7	3.4	5.9	5.8	10.0	4.2	7.2	2.3	4.2	9.5	16.4	1.5	2.6
6	73.1	41.55	56.9	7.2	9.8	6.3	8.7	4.2	5.7	2.4	3.3	9.8	13.4	1.6	2.2

As can be seen, the reaction is accompanied by the formation of almost all possible chloro derivatives of ethylene (with the exception of perchloroethylenes). Among all the by-products, the largest specific proportion is accounted for by dichloroethane, the amount of which ranges from 6 to 16%. In addition to the indicated products, the condensate usually contains a small amount (0.5–2%) of ethylene. Part of the vinyl chloride is carried away with the exiting gas stream, i.e., in the unreacted ethylene the amount of this vinyl chloride ranges from 15 to 20%.

Experimental Part

It is difficult to draw any conclusion concerning the yield of vinyl chloride. In any case, in individual experiments the yield of vinyl chloride reaches 75–77%, calculated on the ethylene that reacted. The same can be said about the conversion of ethylene.

Fig. 1. Diagram of the preparation of vinyl chloride by chlorination of ethylene in a fluidized catalyst bed. 1 —gas meters, 2 —silica gel, 3 —mercury manometer, 4 —manometer, 5 —dust separator, 6 —scrubber, 7 —condenser-cooler

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The ethylene used had a purity in the range of 98-99%. The synthesis of vinyl chloride was carried out according to the following scheme: ethylene and chlorine, after passing through measuring instruments and dryers, entered a reactor charged with pumice (100 mesh fraction) (Fig. 1). The temperature inside the reactor was maintained at 450° ($±$5); the exiting gas mixture passed through a dust separator to a scrubber. After being separated from hydrogen chloride and passing through a cooler, the light fraction was condensed in three successively connected traps at a temperature of 65-70°. Ethylene that had not entered into reaction, after first being passed through gas counters, was discharged into the atmosphere. Every 15 min, two liters of the off-gas were taken for determination of the amount of vinyl chloride being carried away.

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Note: Figure translations are in progress. See original paper for figures.